PB-243 370

REMOVAL OF CHROMIUM FROM PLATING RINSE WATER USING ACTIVATED CARBON

Richard B. Landrigan, et al

Battelle Memorial Institute

Prepared for:

National Environmental Research Center

June 1975

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. PB 243 370
EPA-670/2-75-055		

4. TITLE AND SUBTITLE	5. REPORT DATE
REMOVAL OF CHROMIUM FROM PLATING RINSE WATER USING ACTIVATED CARBON	June 1975 (Issuing Date)
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Richard B. Landrigan and J. B. Hallowell	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle Memorial Institute Columbus Laboratories 505 King Avenue Columbus, Ohio 43201	10. PROGRAM ELEMENT NO. 1BB036 (ROAP 21AZO, Task 17) 11. CONTRACT/GRANT NO. S-802113
12. SPONSORING AGENCY NAME AND ADDRESS National Environmental Research Center Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED Final 14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Chromium is a major pollutant in wastewaters from some electroplating operations. It can be effectively removed from rinse waters by adsorption on activated carbon, which must be regenerated when saturated with chromium to its upper limit. This study was concerned with the best means of regenerating the carbon under conditions which would return it as closely as possible to its original adsorptive capacity. The tests were conducted (1) on a laboratory scale to determine the effects of basic and acidic media on regeneration of chromium-loaded activated carbon and (2) in a small pilot plant unit on the basis of the best results of the laboratory-scale work. In the latter case, tests were conducted on the unit operation for eight adsorption-desorption cycles. The overall results of this study suggest that a chromium removal unit could be installed in many of the small plating plants, relieving the burden on municipal sewage systems, and bringing the plating plant into compliance with local and Federal regulations. Recommendations for improvement of the regeneration process are given even though the process could be used in its present stage of development.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Activated carbon, *Activated carbon treatment, Adsorbents, *Adsorption, Chemical removal (water treatment), *Plating, *Electroplating, Industrial wastes, Metal coatings, *Metal finishing, *Waste recovery, *Waste treatment, Waste water, Chromium	Rinse water	13B

PRICES SUBJECT TO CHANGE

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	54
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	$4.25

EPA Form 2220-1 (9-73)

☆ U.S. GOVERNMENT PRINTING OFFICE 1975-657-594/5401 Region No. 5-11

EPA-670/2-75-055
June 1975

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By

Richard B. Landrigan and J. B. Hallowell

Battelle Memorial Institute
Columbus Laboratories
Columbus, Ohio 43201

EPA Grant No. S802113
Program Element No. 1BB036

Project Officers

Donald Wilson (Cincinnati) and John Ciancia (Edison)
Industrial Waste Treatment Research Laboratory
Edison, New Jersey 08817

NATIONAL ENVIRONMENTAL RESEARCH CENTER
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise, and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

As part of these activities, the efforts on this study have been directed toward an assessment of techniques for regenerating activated carbon used in removing chromium from metal finishers' wastewater. This assessment has been a part of continuing efforts to develop more economical and simpler methods for treating the wastewater from small metal finishing establishments.

A. W. Breidenbach, Ph.D.
Director
National Environmental
Research Center, Cincinnati

ABSTRACT

Activated carbon is highly effective in adsorbing chromium from the rinse water, and leaves no detectable chromium in the water until the carbon is "saturated" with chromium to its upper limit. Thus, it is necessary to "regenerate" the carbon by removing the chromium from it, after which the carbon can be used for another adsorption cycle.

These studies were conducted (1) on a laboratory scale to determine the effects of basic and acidic media regeneration of chromium-loaded activated carbon especially as it affects adsorption capacity of the carbon after repeated cycling and (2) in a small pilot-plant unit on the basis of the best results of the laboratory-scale work. In the latter case, studies were conducted on the unit operation for eight adsorption-desorption cycles.

In the initial laboratory work, experiments were performed to evaluate the use of acidic or basic solutions for removal of chromium from the carbon. Since the basic solution (NaOH) proved more effective, further work was done using caustic. Further work with the basic solutions included a study of adding chelating agents to improve the effectiveness of the regeneration.

Laboratory experiments involving regeneration of chromium-loaded activated carbon in the basic media were conducted in (1) a 5 percent Na_2CO_3 solution, (2) a 20 percent NaOH solution, and (3) a 20 percent NaOH solution containing disodium salt of ethylenediaminetetraacetic acid (EDTA) chelating agent. Chelating agent in amounts ranging from 0.25 g/l to 10 g/l were used in the regenerants. Results of these tests indicated that Na_2CO_3 was not as good a regenerating agent as 20 percent NaOH solution, and that 20 percent NaOH containing chelating agent was a better regenerating agent than 20 percent NaOH when used alone. A regeneration solution of 20 percent NaOH containing 500 mg/l EDTA was selected for use in the pilot-plant runs.

In the pilot plant experiments the capacity of the carbon to adsorb chromium from rinse water varied in the first five cycles but appeared to stabilize in the fifth to eighth cycles. A larger number of cycles would be needed to determine longer-term behavior. During the pilot plant work, it was found that an aeration step more than doubled the effectiveness of the caustic solution for the removal of the chromium from the carbon.

This report was submitted by Battelle's Columbus Laboratories in fulfillment of U. S. Environmental Protection Agency Grant S802113 to Metal Finishers' Foundation. Work was completed as of February 28, 1974.

CONTENTS

		Page
Abstract		iv
List of Figures		vi
List of Tables		vii
Acknowledgements		viii
Sections		
I	Conclusions	1
II	Recommendations	2
III	Introduction	4
IV	Experimental Work	8
V	Appendixes	33

FIGURES

No.		Page
1	Adsorption Capacity for Total Chromium after Multiple Cycles with Acid (5 percent H_2SO_4) Used for Stripping	11
2	Adsorption Capacity for Total Chromium after Multiple Cycles with Basic Stripping Media	12
3	Adsorption Capacity for Total Chromium after Multiple Cycles with NaOH Stripping Solution (Effect of EDTA Concentration)	13
4	Adsorption Capacity for Total Chromium after Multiple Cycles with NaOH Stripping Solution	14
5	Chromium Retained on Carbon after Adsorption-Desorption Cycles	17
6	Schematic Diagram of Activated Carbon Adsorption Unit	18
7	Results of Experiments During an Eight Cycle Operation of the Pilot-Plant Unit	22
8	Concentration of Chromium in Wash Solutions	25
9	Chromium Loading Remaining on Carbon after Regeneration	26
A-1	Standard Chromium Curve	35

TABLES

No.		Page
1	Data from Experiment Nos. 4, 6, and 8	15
2	Capital Costs for Continuous Treatment of Chromium Rinse Waters	29
3	Operating Cost Estimate for Continuous Chrome Removal by Conventional Process	30
B-1.	Summary of Data from Laboratory Experiments on Chromium Adsorption and Regeneration Using Acid and Basic Media	36
C-1	Summary of Regeneration Operation Data	39
D-1	Data on Results of Eight Cycles of Operation in the Pilot-Plant Unit	43

ACKNOWLEDGMENTS

This project represents the cooperative effort of the U. S. Environmental Protection Agency, the Metal Finishers' Foundation, and Battelle's Columbus Laboratories. This study was performed under EPA Grant S802113 to the Metal Finishers' Foundation, under which were combined the efforts of the Pollution Abatement Committee of the Foundation, represented by E. P. Durkin, and the cooperation of the Superior Plating Company, Columbus, Ohio, represented by James Shriver, at which plant the chromium removal equipment was installed and operated. Experimental work was performed in the laboratory and in the plant by Battelle-Columbus staff members including R. G. Brown, T. L. Tewksbury, and R. B. Landrigan, with project supervision by G. R. Smithson, Jr.

SECTION I

CONCLUSIONS

(1) Chromium can be adsorbed by activated carbon from rinse water solutions up to a concentration of at least 600 mg/l.

(2) Chromium can be desorbed from activated carbon using a cycle of (a) wetting with 20 percent NaOH-500 ppm chelating agent solution, (b) exposing the wetted carbon to air for 18 hours, (c) washing with 20 percent NaOH solution, (d) washing with water, (e) washing with sulfuric acid solution.

(3) The process stabilized after eight cycles where about 6-1/2 pounds of chromium remained on the carbon after the acid wash (see Figure 7) and where a total loading of 16 pounds of chromium was reached after adsorption (based on 200 pounds of activated carbon).

(4) The majority (over 90 percent) of the chromium adsorbed was removed in the caustic-aeration and water wash steps.

(5) A maximum loading of 22 pounds of chromium (per 200 pounds of carbon) was reached in one cycle.

(6) Under actual plant operating conditions of 20 gpm of rinse water containing 100 ppm of hexavalent chromium, an activated carbon system would require a capital investment of approximately $35,800. Under these conditions, the estimated total operating cost would amount to about $62.60 per day. This includes the cost of disposing of the regenerant.

SECTION II

RECOMMENDATIONS

In this program an evaluation of a process for treatment of chromium rinse waters was continued. It is recommended that field tests be conducted using the same activated carbon process and following the same procedure outlined in this report. To realize the full potential of this process, the data should be extended to include a large number of cycles, at various sites having different rinse solution compositions.

It also is recommended that a laboratory program be conducted concurrently with the field tests to resolve some of the basic questions raised in the pilot-plant operation. These include:

(1) The solubility of the chromium compounds of interest in caustic solutions varying from 0 to 20 percent NaOH at various temperatures from 80 to 180 F

(2) The solubility of the chromium compounds of interest in various sulfuric acid solutions ranging from pH 1.5 to 6.5 at various temperatures

(3) The best oxidizing agent to use. Those suggested are air, hydrogen peroxide, sodium peroxide, oxygen, ozone, etc.

(4) How the caustic wash solution should be handled to obtain optimum desorption. For example,

   a. first 30 gallons once-through, second 30 gallons recycled

   b. all recycles

   c. all once-through

(5) How best to prepare carbon with acid wash

   a. contact with strong acid

   b. contact with weak acid

   c. what temperature to contact with acid

(6) What method is best for recovery of chromium from wash solutions and its ultimate disposal.

Answers to the following questions should come from the experimental work:

(1) Can a maximum value of adsorption be attained in each cycle? In the eight cycle operation described here a maximum value of 22 pounds of chromium was adsorbed on 200 pounds of carbon.

(2) Why was the maximum loading not achieved every time? Did the fast addition of acid change the carbon so that more chromium was adsorbed?

(3) Can the adsorbed chromium be stripped more effectively if the chromium is oxidized? Does the improved stripping technique lend itself to better adsorption capacity? To what extent will the improved stripping and higher adsorption capacities enhance the practical and economic feasibility of the process?

(4) What is the effect of more dilute chromium rinse solution on adsorption and on desorption? What effect do metals such as Ni, Cu, Zn, etc., have on the adsorption-desorption cycle, and what is the maximum tolerance of the carbon-absorption system for such contaminants?

The answers to these questions from either the laboratory or the field should make the process more versatile so that it could cover a variety of situations met in the small plating plants located throughout the nation.

SECTION III

INTRODUCTION

The work presented in this report represents the latest segment of a series of studies involving the cooperative efforts of the U.S. Environmental Protection Agency, the Metal Finishers' Foundation, and Battelle's Columbus Laboratories. These studies have extended over the last several years and have included, in serial order, a state-of-the-art survey of metal finishing wastewaters, evaluation of numerous treatment methods for various wastewaters, and laboratory work on treatment of selected types of wastewaters, most notably those containing cyanides and those containing chromium. During the evaluations of various treatment systems, emphasis has been placed on identifying systems applicable to smaller plating operations.

Reports of the earlier work are identifiable as:

> "A State-of-the-Art Review of Metal Finishing Waste Treatment"; U.S. Department of the Interior, Federal Water Quality Administration; Water Pollution Control Research Series, 12010 EIE 11/68
>
> "An Investigation of Techniques for Removal of Chromium from Electroplating Wastes"; U.S. Environmental Protection Agency, 12010 EIE 03/71
>
> "An Investigation of Techniques for Removal of Cyanide from Electroplating Wastes", U.S. Environmental Protection Agency, 12010 EIE 11/71.

In these earlier reports, background information including a state-of-the-art study and current practices in small electroplating plants was presented. Production characteristics and waste effluent volumes and composition were discussed. In the previous experimental work nonconventional methods of treatment of chromium rinse waters studied included ion flotation, liquid-liquid extraction, activated carbon adsorption, activated alumina adsorption, reverse osmosis and reduction with activated carbon. A preliminary estimation of costs of the various methods was also given.

Carbon adsorption was singled out as the most promising method to study. As a result, experiments were performed with both acid regeneration and caustic regeneration. Results of the acid regeneration experiments showed that this media was not completely effective in stripping chromium once it had been adsorbed on the carbon.

Results of the caustic regeneration (followed by an acid wash treatment to remove residual caustic and condition the column for subsequent adsorption cycles) indicated that chromium adsorption capacities were somewhat better than with acid regeneration.

The results of those preliminary studies demonstrated that electroplating plant rinse waters could be effectively treated with activated carbon, but that important areas existed for additional study or refinement of the process.

The work on chromium removal methods thus has reached the stage described in this document; namely, the operation of a carbon adsorption system for the treatment of rinse waters from a commercial chromium plating operation. This study thus represents work on the stage of development of the transition from laboratory bench to plant application.

The objectives of this program were to achieve a timely assessment of the practicability of this system within a limited program. This included the judicious selection of operating conditions and determining the effectiveness of the system under actual operating conditions in the plant. The overall timing of the program was affected by plant operations in that a seasonal shutdown of the chromium plating line was spanned by this program.

Report Content

The following sections of the report deal with two separate types of work:

(1) laboratory bench studies

(2) operation of a pilot scale device in a plating plant.

The laboratory bench studies were performed to allow the determination of the choice of whether acid or caustic should be used to strip or remove chromium from the activated carbon, and, once caustic was selected, whether either stripping or the subsequent adsorption capacity could be enhanced by the addition of a chelating agent to the caustic.

The operation of the pilot-scale unit to remove chromium from rinse waters in a plating plant was carried out to determine the effectiveness of the unit under real plant conditions. The original concept was to operate for 100 cycles of the adsorption-strip-reactivate sequences to determine the effective life of the carbon and to determine carbon losses (i.e., operating and maintenance costs). Final contract limitations and plant operating conditions combined to limit operations to eight cycles.

Overall Description of Operating Sequence and Explanation of Terms

The generalized sequence of operations associated with the removal of chromium from waste waters by carbon absorption may be described as consisting of two major sequences:

(1) Adsorption - during which chromium-rinse waters are passed over activated carbon and the chromium is adsorbed onto the carbon. The carbon eventually becomes loaded with chromium to some limit, whereupon adsorption ceases, and, if flow is continued, the effluent still contains chromium.

(2) Regeneration - during which the carbon is treated by passing, for example, caustic (NaOH) solution over the carbon to remove the chromium from the carbon and restore the adsorbing capacity of the carbon. This major cycle actually consists of the following steps:

   (a) Desorbtion - caustic is run through the carbon to remove the adsorbed chromium

   (b) Water is run through the carbon to rinse away any residual caustic

   (c) Acid is run through the carbon to restore the carbon to the pH condition necessary for best adsorption

   (d) Water is run through the carbon to rinse away any residual acid. The carbon is then ready for another cycle of adsorption, i.e., (1) above.

Thus it may be seen that the laboratory work was aimed at the refinement of step 2a, whereas the pilot-plant work necessarily dealt with all steps of the operation.

The characteristics of operation of the activated-carbon-adsorption apparatus are that during the adsorption cycle, all the chromium is removed from the waste rinse water put through the carbon. For example, the plating plant rinse waters treated in this study contained analyzed values of up to approximately 600 mg/l of chromium. After passing through the carbon, the water would contain no detectable concentration (< 0.05 mg/l) of chromium.

When the adsorption capacity of the carbon was reached or exceeded, (during operations in the plant) the effluent exhibited a corresponding change from colorless to a light yellow, or tan, or brown color characteristic of this particular rinse water. This change, which was termed "break-through", was readily detected with the unaided eye, and was confirmed by analytical results.

The prior results focused additional efforts on the area of apparent loss of adsorptive capacity after multiple cycles of operation with either caustic or acid stripping to determine the reason for the loss of adsorptive capacity and to determine how to maintain it at a high level. A less important aspect of the process involves complete

stripping of the adsorbed chromium from the carbon during the regeneration cycle. Incomplete stripping occurred during all runs. Whether adsorption capacities could be increased significantly if complete stripping were achieved remained to be established. This phase of the operation would require further study. Since reduction of chromium during adsorption was found to occur and since this material would be stripped very slowly during the regeneration cycles, a chelating reagent (EDTA*) was added in new experiments to aid in the release of tightly bound chromium. Hence experiments were performed in BCL laboratories on a small scale and at Superior Plating Company, Columbus, Ohio, on a pilot scale to test the effectiveness of this addition to improve the stripping of chromium from the carbon.

The pilot plant was operated over a 3-1/2-month period where eight cycles of adsorption-desorption were performed on a bed of activated carbon.

* Disodium salt of Ethylenediaminetetraacetic acid

SECTION IV

EXPERIMENTAL WORK

The experimental program was divided into two areas. The first was laboratory studies of adsorption of chromium in a stirred bed of carbon at a fixed pH of the solution followed by the desorption of chromium using (1) 5 percent H_2SO_4 solution, (2) 5 percent H_2SO_4 plus sodium persulfate, (3) 5 percent H_2SO_4 plus chelating agent, (4) 20 percent sodium hydroxide, (5) 20 percent sodium hydroxide plus chelating agent, and (6) 5 percent ammonium carbonate.

The second was pilot-plant studies of the adsorption of chromium on activated carbon, the desorption of the chromium with 20 percent NaOH-chelating agent (500 ppm) solution, and the reactivation of the carbon with H_2SO_4 solution.

Laboratory Experimental Work

The initial conditions selected for laboratory studies were based on the findings of previous work in which various grades of carbon were evaluated and various conditions, such as optimum pH of the carbon, were determined[1,2,3]. These prior studies established the basis for the selection of Pittsburgh OL activated carbon (denoted as a granular-type carbon with a particle size of 20 x 50 mesh). Similarly, maximum chromium-removal was achieved in the prior work using carbon treated to a pH of 3.

The chromium-containing rinse water used in the laboratory experiments was obtained from the rinse-water tank of the same plating shop where the pilot-plant work was to be done. This solution ranged in total-chromium content from 0.234 g/l to 0.315 g/l during the experiments (see Table B-1, Appendix B). The chromium-rinse water obtained from the plant consisted of make-up water from the local municipal supply plus constituents introduced by chromium-plate-rinse operations. Rinse waters from other (e.g., brass-) plating operations were excluded from this work.

Laboratory experiments were conducted wherein acid and basic solutions with and without chelating agent were used to determine the best desorption agent. The experiments were conducted in five or more cycles. The procedure included washing a 5-gram sample of carbon with acid to adjust the pH to 3.0 prior to adsorption.

The carbon was then stirred for 1 hour in one liter of chromium-plating rinse water. The pH was adjusted by the addition of H_2SO_4 to maintain a value of 3.0 during adsorption. The mixture was filtered and the filtrate analyzed for hexavalent and total chromium. The methods of analyses are outlined in Appendix A. The filtered carbon was regenerated in one liter of stripping solution by stirring for 1 hour. (This ratio of carbon to solution was much smaller than in the subsequent pilot-plant operations, 5 g/l versus 200 pounds/30 gallons = 1140 g/l.) The mixture was filtered and the filtrate analyzed. The results of these experiments are tabulated in Appendix B.

Three regeneration experiments were conducted using an acid solution and eight regeneration experiments were conducted using a basic solution as listed below.

Experiment	Stripping Solution
1	5 percent H_2SO_4
2	5 percent H_2SO_4 + 10 g/l EDTA*
3	5 percent H_2SO_4 + 10 g/l ammonium persulfate
4	20 percent NaOH
5	5 percent $(NH_4)_2CO_3$
6	20 percent NaOH + 10 g/l EDTA*
7	20 percent NaOH + 5 g/l EDTA*
8	20 percent NaOH + 1 g/l EDTA*
9	20 percent NaOH + 0.5 g/l EDTA*
10	20 percent NaOH + 0.25 g/l EDTA*
11	20 percent NaOH + 0.1 g/l EDTA*

The results of these experiments are shown graphically in Figures 1, 2, 3, and 4.

Discussion of Results of Laboratory Experiments

Results of the first three experiments (details listed in Appendix B) indicate that the quantity of chromium adsorbed decreased as the number of cycles increased, suggesting that the carbon would be spent and require rejuvenation or replacement after only a few additional cycles. It can be seen from the graphs in Figure 1 that the use of the oxidant ammonium persulfate in the acid stripping solution resulted in a relatively faster decline in absorptive capacity of the carbon. The data for the sixth through ninth cycles of Experiment 2 show anomalous behavior, which is tentatively attributed to varying storage times applicable to the latter cycles.

The results using a basic solution for stripping indicate that the 5 percent ammonium carbonate causes rapid degeneration of the adsorption capacity of the carbon after five cycles, as shown graphically in Figure 2 (Experiment 5). Whether the adsorption capacity could be recovered in subsequent cycles was not determined. In any event, the use of ammonium carbonate would be no better than caustic solution.

* Disodium salt of ethylenediaminetetraacetic acid

Results of experiments with addition of chelating agent to the caustic stripping medium show, by a comparison of Figures 2, 3, and 4, that the highest total chromium adsorbed after five cycles was 0.045 g/g carbon when 10 g/l of EDTA was used (Experiment No. 6) and the lowest total chromium adsorbed after five cycles was 0.038 g/g carbon when 1 g/l of EDTA was used (Experiment No. 8). Total chromium adsorption values for carbon stripped with 20 percent caustic solution containing in the range of 0.1 g/l to 5 g/l EDTA fall within a value of 8 percent above the lowest total adsorption values. It was concluded that the effectiveness of chelating agent in removing proportionate quantities of chromium dropped as the quantity of chelating agent increased. Effectiveness is based on the ratio of EDTA and quantity of chromium removed in excess of that removed in caustic solution alone. A comparison of Experiments 4, 6, and 8, presented in Table 1, suggests the trends noted in the data, i.e., the adsorption capacity of the carbon appeared to be better sustained with 10 g/l of EDTA (Experiment 6) while the residual chromium appeared to be simultaneously higher. These data appeared to indicate some benefit from the addition of EDTA. The cumulative chromium retained on the carbon after each cycle for each experiment is presented graphically in Figure 5, showing the effects of stripping and regeneration. These data again suggest some benefit from the addition of intermediate amounts of EDTA, although the effect is not totally decisive.

For example, the values for percent of chromium adsorbed given show higher sustained values at the five cycle point for Experiment 6 (10 g/l EDTA) than for experiments with smaller amounts of EDTA. Similarly, the data plotted in Figure 5 show a striking difference of behavior between Experiment 8 (1 g/l EDTA) and Experiment 1 (no EDTA) beyond the five-cycle point.

Pilot-Scale Work

Before discussing the actual experiments and data accumulated in the pilot-plant work a description of the facility and the general procedure followed is presented.

Design of Equipment

The experimental unit (a Standard Ion Exchange package purchased from the Illinois Water Treatment Company) was essentially as shown in Figure 6. The major equipment items are (1) a 30-gallon galvanized rinse tank sump, (2) two 1000-gallon rubber-lined storage tanks, (3) two 30-gallon polyethylene makeup tanks, and (4) two 12-inch-diameter by 6-feet high rubber-lined adsorption columns, each containing 100 pounds of activated carbon. All the piping and valves are polyethylene.

The liquids are transported through the system by four chemical-resistant centrifugal pumps. The rinse-water pump delivers the rinse water from the overflow rinse tank (sump) to the storage tank. This pump is activated and deactivated by a microswitch attached to a float in the sump tank. The stored rinse water is recycled in the storage

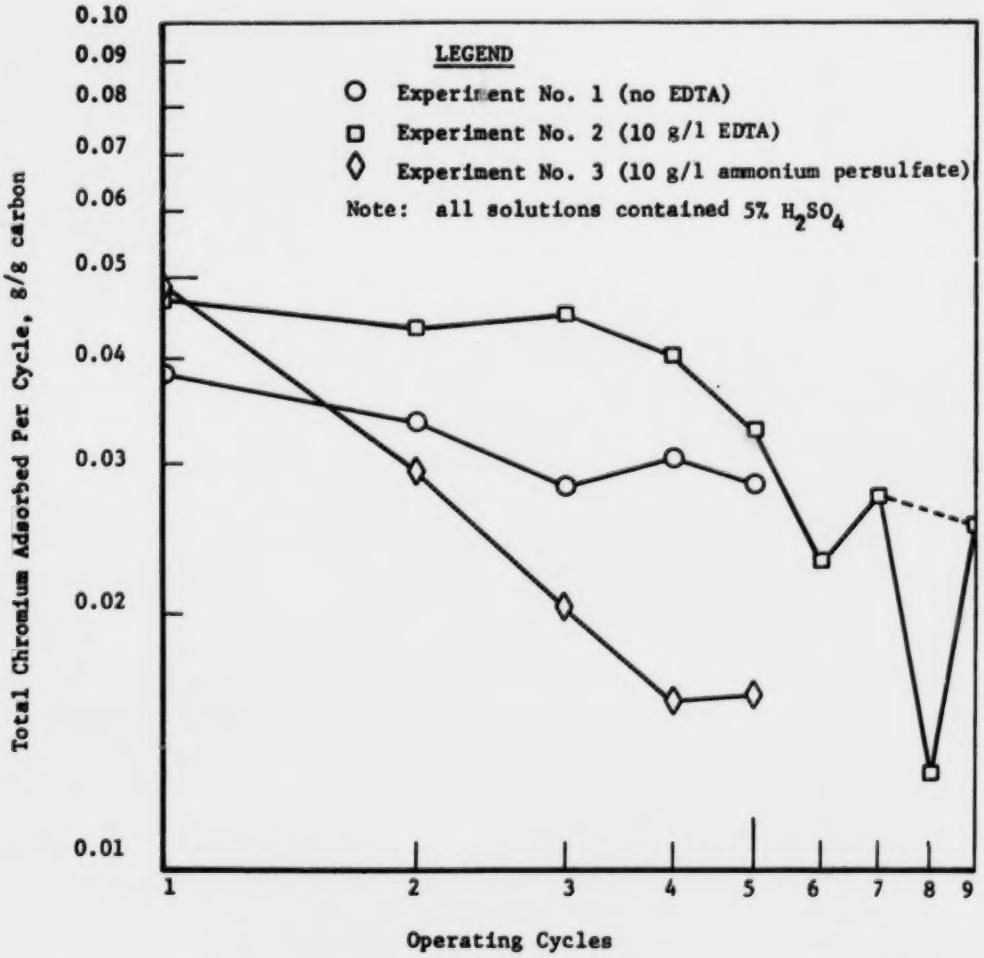

FIGURE 1. ADSORPTION CAPACITY FOR TOTAL CHROMIUM AFTER MULTIPLE CYCLES WITH ACID (5 PERCENT H_2SO_4) USED FOR STRIPPING

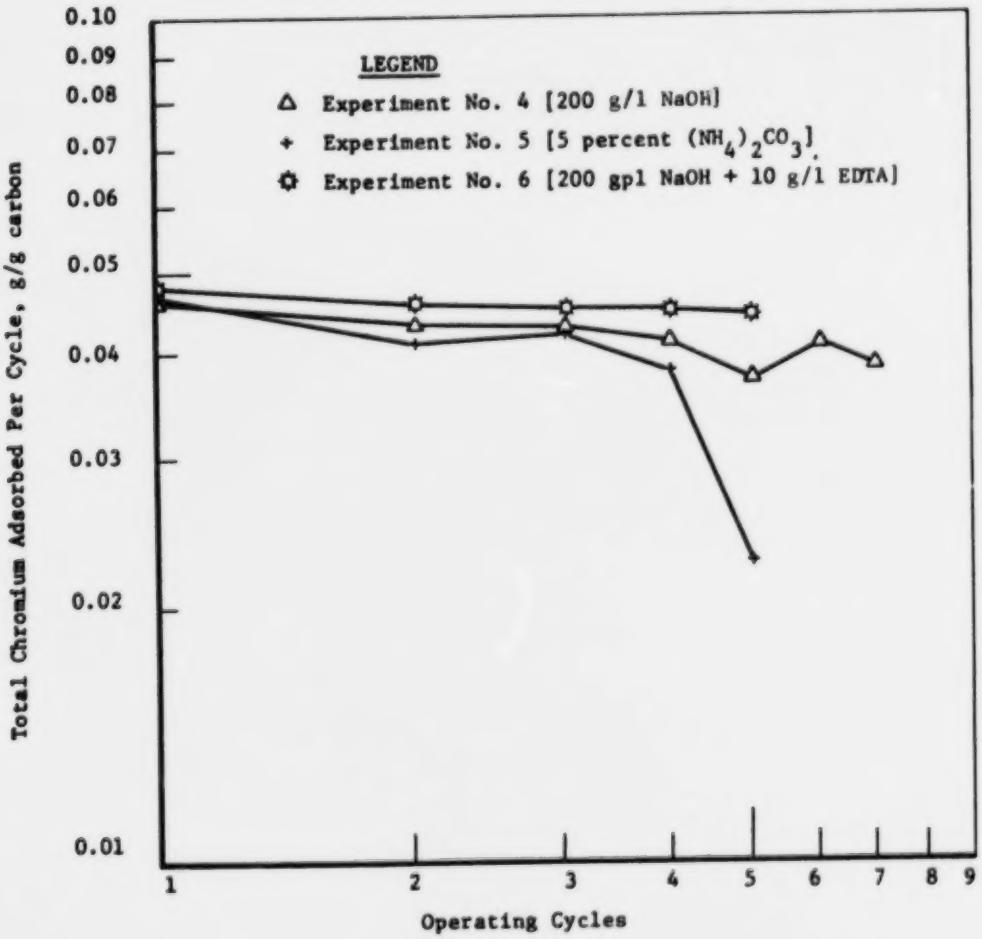

FIGURE 2. ADSORPTION CAPACITY FOR TOTAL CHROMIUM AFTER MULTIPLE CYCLES WITH BASIC STRIPPING MEDIA

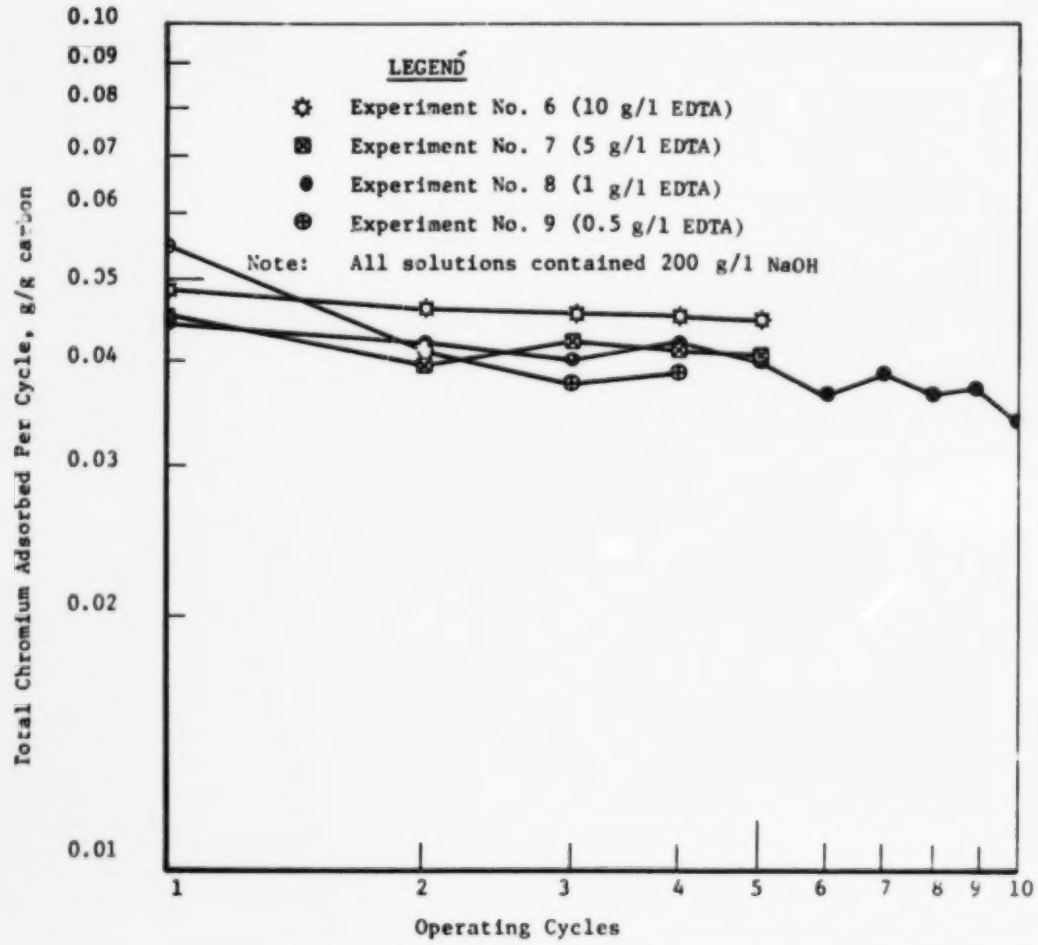

FIGURE 3. ADSORPTION CAPACITY FOR TOTAL CHROMIUM AFTER MULTIPLE CYCLES WITH NaOH STRIPPING SOLUTION (EFFECT OF EDTA CONCENTRATION)

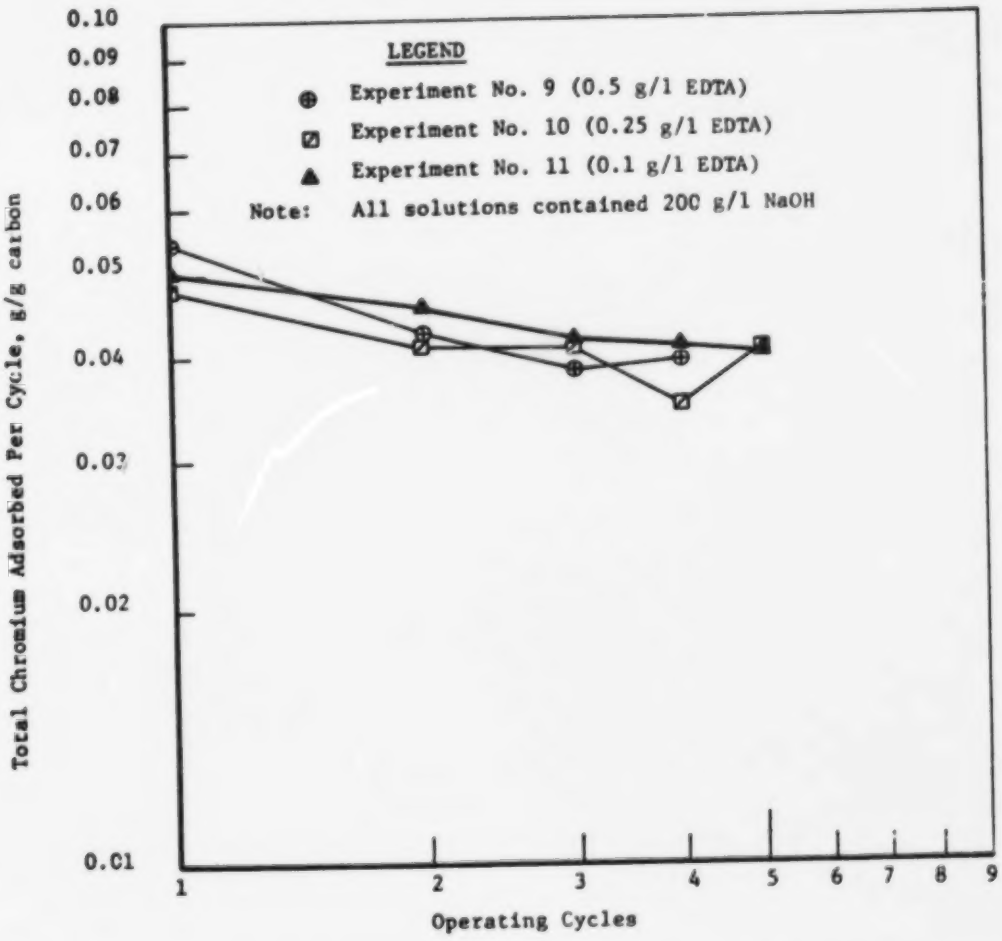

FIGURE 4. ADSORPTION CAPACITY FOR TOTAL CHROMIUM AFTER MULTIPLE CYCLES WITH NaOH STRIPPING SOLUTION (EFFECT OF EDTA CONCENTRATION)

TABLE 1. DATA FROM EXPERIMENT NOS. 4, 6, and 8

Cycle	Experiment No. 4 (stripping solution 20% NaOH, no EDTA)	
	Total Chromium Adsorbed from Rinse Water, percent	Chromium Remaining on Carbon (cumulative total), grams total Cr/grams carbon
1	79	0.006
2	74	0.01
3	73	0.02
4	70	0.01
5	64	0.01
6	65	0.02
7	63	0.02
8	--	--
9	--	--
10	--	--

Cycle	Experiment No. 6 (stripping solution 20% NaOH, 10 g/l EDTA)	
	Total Chromium Adsorbed from Rinse Water, percent	Chromium Remaining on Carbon (cumulative total), grams total Cr/grams carbon
1	79	0.01
2	75	0.02
3	73	0.03
4	73	0.03
5	72	0.03
6	--	--
7	--	--
8	--	--
9	--	--
10	--	--

TABLE 1. CONTINUED

Cycle	Experiment No. 8 (stripping solution 20% NaOH, 1 g/l EDTA)	
	Total Chromium Adsorbed from Rinse Water, percent	Chromium Remaining on Carbon (cumulative total), grams total Cr/grams carbon
1	75	0.01
2	72	0.009
3	67	0.006
4	68	0.01
5	67	0.01
6	59	0.006
7	63	-0.004
8	60	-0.006
9	61	-0.006
10	55	-0.007

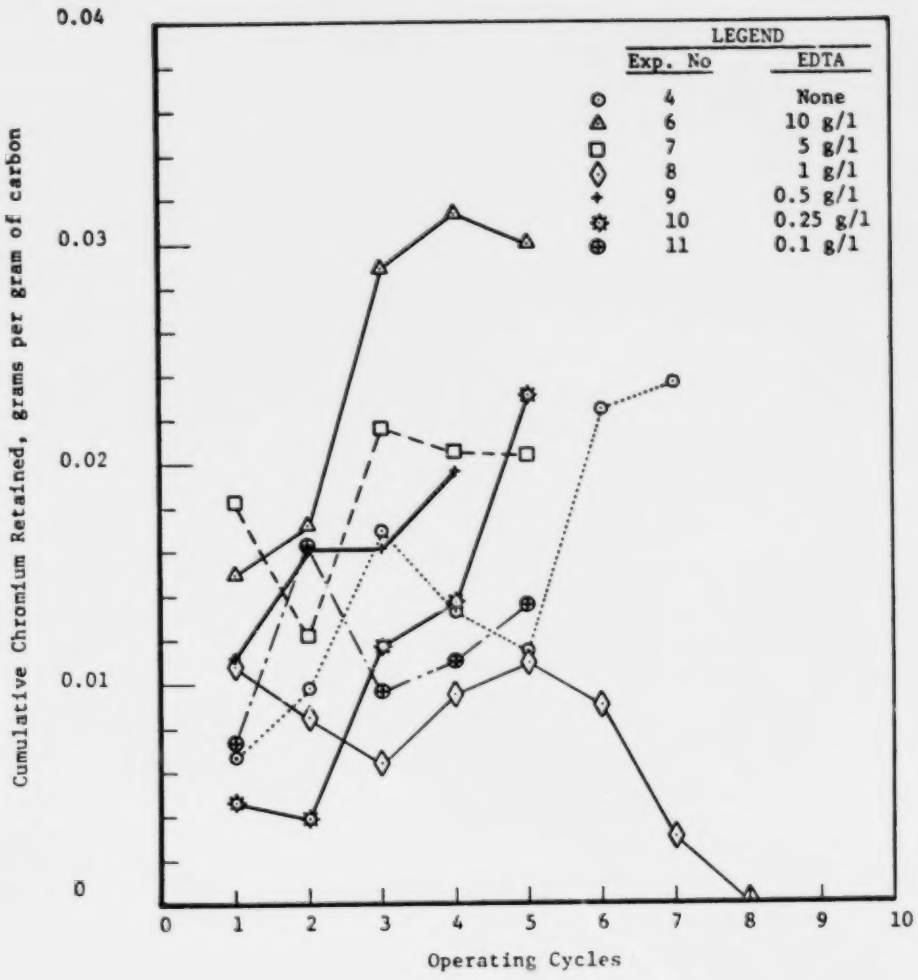

FIGURE 5. CHROMIUM RETAINED ON CARBON AFTER ADSORPTION-DESORPTION CYCLES

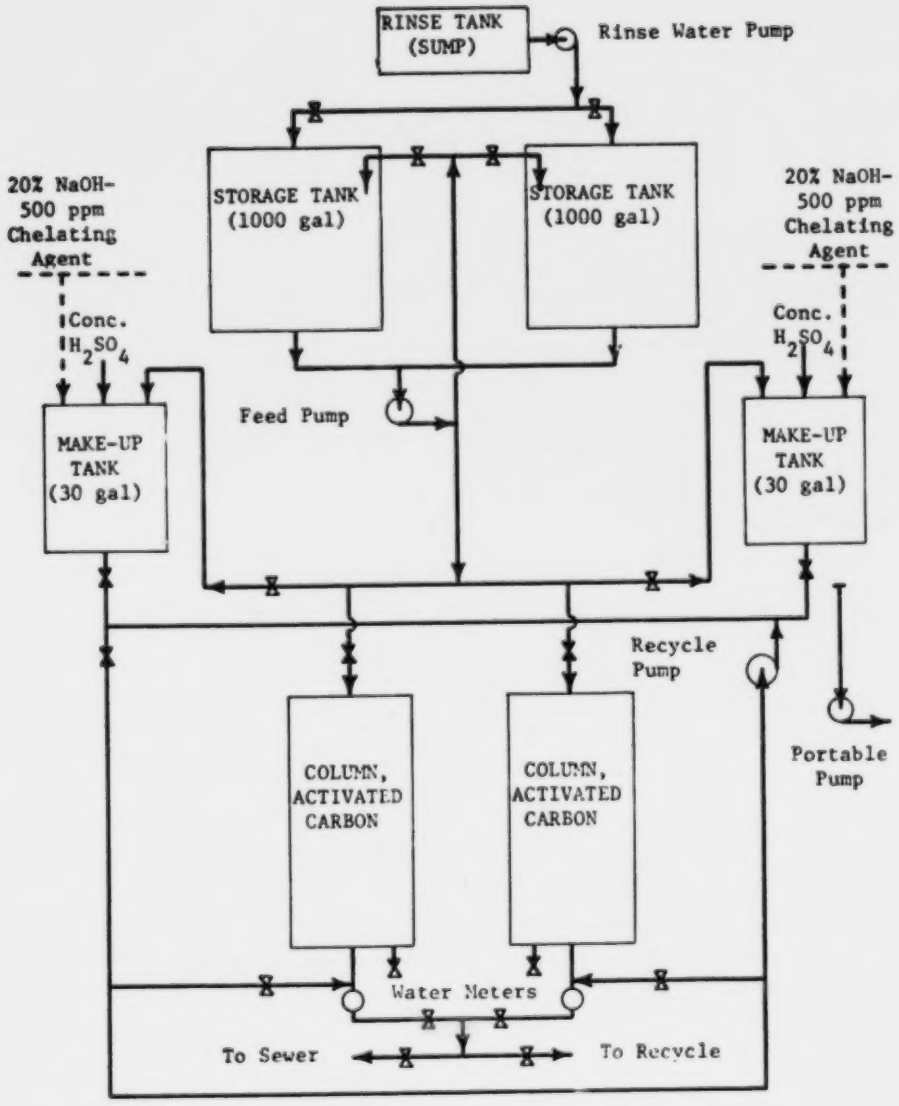

FIGURE 6. SCHEMATIC DIAGRAM OF ACTIVATED CARBON ADSORPTION UNIT

tanks and/or fed to the top of the activated carbon adsorption towers where the chromium is removed. The clean metered effluent water is returned to the rinse tanks for reuse. When the activated carbon is loaded with chromium compounds, as revealed by the discoloration and pH change of effluents at breakthrough, the adsorption is terminated and regeneration begins. Regenerating solutions and wash solutions are cycled through the columns in an upward direction via the recycle pump. Spent regeneration solutions and wash solutions are transferred from the makeup tank to the sewer or neutralizing/settling vessel via the portable pump.

The two-column design allowed for an optional procedure of regenerating one column while the other was being used for absorbing chromium. Since chromium-rinse operations were non-continuous, this mode of operation was not considered appropriate.

The sump tank serves to catch and transfer rinse water overflowing from the chrome-rinse bath, which was, in this particular case, operated as a running-water rinse, i.e., tap water was allowed to run into the tank continuously while the plating line was operating. This flow was varied by the plating line operators depending on production conditions. The liquid level control points in the 30-gallon sump were set at any convenient levels which would avoid overflow and avoid running the pump when there was no solution in the sump. The sump allowed the automatic collection of rinse water in the storage tanks until sufficient supply was available to justify an adsorption cycle.

The feed pump was used to mix the accumulated solutions (by pumping from both back into both) in order to more nearly equalize the feed to the columns during this experimental work.

In the particular work described, regenerating solutions were made up sequentially in the makeup tanks, i.e., the caustic solution was prepared, circulated through the columns, and then drained away, then acid solution made up and drained away, etc.

Any installation for long-term operation should naturally incorporate chemical supply or storage tanks.

Procedure

The carbon when first put in the columns is prepared for an adsorption cycle by treating with sulfuric acid solution until a pH of 3 is reached. This is accomplished by adding concentrated sulfuric acid at the rate of 200 ml/min to 30 gallons of water which is cycling through the activated carbon column in series with the makeup tank. When a pH of 3 is reached, the acid is recycled for a period of 60 minutes and then drained from the column into the sewer or neutralizing vessel. The acid volume is measured and a sample of the solution analyzed for chromium. The remaining acid is blown out of the column and into the makeup tank with air entering the top of the column. The column is ready now for the next adsorption run.

Each column is flushed with 30 gallons of water and the effluent is analyzed for chromium. Plating rinse water containing 200-700 mg/1 chromium is pumped through the activated carbon column in a downflow direction at a rate of 2 to 3 gallons/minute/column. The two columns are operated in parallel and effluent flowing from the column is monitored with water meters reading in gallons. Spot checks are made to maintain approximately equal rinse water flow rates through each column. When a breakthrough of the column is observed as evidenced by pH of the effluent rising above 6 or the color changing to a pale yellow, the adsorption phase of the cycle is terminated.

The column is drained and the regeneration is begun. The activated carbon is washed with 30 gallons of 20 percent caustic solution containing 500 mg/1 chelating agent by cycling the solution (in an upflow direction) through the column and makeup tank in series. After cycling the caustic solution for one hour, the column is drained completely into the makeup tank and held for further washing after an air treatment.

Air is blown slowly through the column in a downflow direction for 18 hours (overnight). The used 20 percent caustic solution is then returned to the activated column and recycled for an additional wash for one hour.

The caustic solution is removed from the system; the volume measured, and the effluent analyzed for chromium.

Each column is washed for one hour with 30 gallons of recycling tap water (in an upflow direction); the effluent is collected, the volume measured, and the solution analyzed for chromium.

The column is again prepared for adsorption by acid washing and the cycle repeated.

A chromium balance of the feed material versus that recovered in the various effluents and/or lost is made.

The sequence of operations may be summarized in chart form as follows:

Operation	Volume	Chemical Content	Time
Acid Wash	30 gallons	5% H_2SO_4	1 hour
Drain	--	--	--
Water Rinse	30 gallons	Tap Water	1 hour
Drain	--	--	--
Cr Adsorption	Variable	200-600 mg/1 Cr	11-3/4 - 19-1/2
Drain	--	--	--
Caustic Strip	30 gallons	20% NaOH+500 mg/1 EDTA	1 hour
Drain	--	--	--
Aerate	--	--	18 hours
Caustic Strip	(Reuse above)		1 hour
Water Rinse	30 gallons	Tap Water	1 hour
Drain	--	--	--

The chromium adsorption cycle is dependent on the concentration of chromium in the rinse water. The adsorption may be expressed in terms of 8 to 9 pounds (the value in 4 of the eight runs) of chromium adsorbed on the 200 pounds of carbon. For example, at a pumping speed of 2 gpm (7.6 l/m), a solution containing 200 mg/l of chromium would be equivalent to 8 pounds of chromium in approximately 40 hours; a solution with 600 mg/l of chromium would be equivalent to 8 pounds of chromium in 1/3 of that time (i.e., 13-1/3 hours).

In the case of the higher concentration (600 mg/l), the volume of rinse water involved would be approximately 1600 gallons, i.e., the 8 pounds of chromium would be transferred from 1600 gallons of rinse water (all of which would be fit for recycle or discharge) to 120 gallons of regenerating and rinse solution, which could be treated for recovery or disposal.

In the above listing, the 18 hours for aeration reflect a convenient, overnight cycle length, and might well be reduced. This and other areas of potential improvement are listed in the Recommendations section of this report.

Pilot-Plant Experimental Work

During a 3-1/2-month period the pilot-scale adsorption unit was operated in the open-loop fashion for eight cycles at Superior Plating Company in Columbus, Ohio, with one exception of three hours when the unit was operated in a closed loop. The general procedure followed in most runs was (1) an acid wash to prepare the carbon bed for adsorption, (2) an adsorption cycle, (3) a short-time 20 percent NaOH-500 ppm chelating agent wash, (4) an aeration of the wetted bed, (5) a short-time wash with the caustic solution used in (3), and (6) a water wash. In three runs the acid wash was followed by a water wash.

The experimental conditions and results of these eight cycles are shown in Appendix C. Some of the results also are shown graphically in Figure 7.

In the acid wash, the carbon was prepared for the adsorption step. Experience in previous runs indicated a pH of 2.8 to 3.2 of the wetted carbon was desirable for good adsorption. The acid was added rapidly to the circulating solution in the first four runs and slowly in the last four runs. Initially it was assumed that the rate of acid addition had no affect on the adsorption capacity of the carbon. However, the results of the first four acid additions suggested that there is an effect on adsorption capacity, especially in cycle 4 where 16 percent chromium was adsorbed (see Figure 7).

Plating rinse solutions used in the experiments were uncontaminated chromium-rinse (i.e., rinses used only on chromium-plated work, in contrast to zinc-plated work, for example) solutions containing a total chromium content in the range of 254 ppm to 608 ppm. The adsorption rate was faster with the more highly loaded solution; however, the total loading changed only slightly with feed chromium concentration.

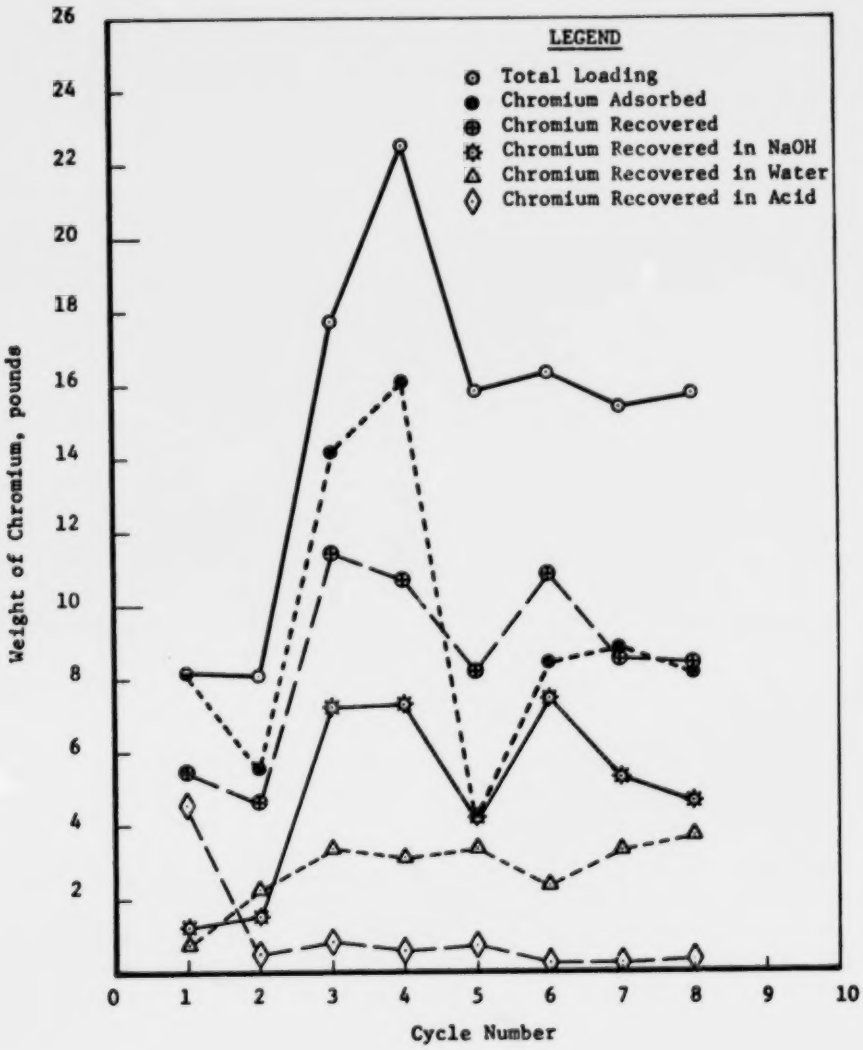

FIGURE 7. RESULTS OF EXPERIMENTS DURING AN EIGHT CYCLE OPERATION OF THE PILOT-PLANT UNIT

The quantity adsorbed per cycle and the total loading of the carbon are shown in Appendix D and Figure 7.

It may be noted that the amount of chromium recovered is higher than the weight absorbed for cycles 5, 6, and 8 in Table D-1 (Appendix D). This is related to the recovery of chromium not stripped in previous cycles. A recovery rate less than 100 percent in the earlier cycles reflects an accumulation of chromium on the carbon, part of which is apparently recovered in later cycles.

The adsorbed chromium was desorbed from the carbon in three washes interspersed with an aeration of the NaOH wetted bed. The loaded bed was washed with 20 percent NaOH solution containing 500 ppm of EDTA chelating agent for periods of 1/4 to 100 hours (see Appendix C). The drained bed was aerated for 14 to 72 hours followed by a continuation of the first wash using the same solution. The aeration step allowed additional chromium to be removed in the NaOH solution.

The caustic wash was followed by a water wash which removed additional chromium.

The water wash was followed by a repeat of the cycle with the acid wash wherein additional chromium was removed.

Results

In the first cycle only 40.5 percent of the adsorbed chromium was removed in two caustic-solution washings. The first wash removed about 18 percent of the adsorbed chromium in 100 hours of washing, which was the same quantity in solution after 1/2-hour of washing. The extra 99-1/2 hours of washing were unnecessary. In a second wash with fresh caustic solution another 22.5 percent of the adsorbed chromium was removed in a 72-hour wash. The remaining chromium was removed by an acid wash followed by a water wash. The water wash removed 51 percent of the chromium adsorbed. Slightly over 50 percent of the adsorbed chromium was recovered. This low desorption value indicated the caustic solution was not performing as expected and for this reason the procedure was changed in subsequent cycles. The change was made based on review of the experimental data.

After the experimental work was completed it was noted that, in a few experiments, a sample of activated carbon left on a filter overnight, exposed to air and wetted with caustic solution (not yet washed with water), showed a greater desorption of chromium than a sample of activated carbon which was processed immediately. The air exposure was not controlled nor was the increased desorption expected. When the benefits of aeration were realized, an aeration step was incorporated in the pilot-scale-desorption procedure.

In the second cycle slightly less chromium was adsorbed and slightly less chromium recovered than in the first cycle. However, the amount of chromium recovered in the caustic solution had increased in weight and the amount of chromium recovered in the water wash had increased

in weight. The combined caustic and water wash in this run accounted for 85 percent of the recovered chromium--35.3 percent in the NaOH solution and 49.5 percent in the water. The rest of the chromium was recovered in the acid wash and a water wash that followed - 9 percent in the acid solution and 6.5 percent in the rinse water.

In the third cycle both the quantity of chromium adsorbed and the quantity of chromium recovered increased. The quantity of chromium adsorbed amounted to almost twice that in Cycle 1. The combined caustic wash and water wash accounted for 93 percent of the total chromium recovered, with the remaining 7 percent recovered in the acid solution. The weight of chromium in the caustic wash was about twice that in the water wash. Repeated alternate washing and aeration with the same solution indicated that the maximum chromium was removed after the first aeration period. A prolonged treatment was not beneficial for chromium removal (see Appendix C). The greater adsorption power of the carbon is though to be due to the manner in which the acid is added - fast or slow.

In Cycle 4 an increased quantity of chromium was adsorbed equal to a loading of .115 g Cr/g carbon. This was the maximum loading of the carbon in these cycles. The combined caustic wash and water wash removed 92 percent of the adsorbed chromium. Additional desorption may be possible because the caustic solution and the water solution apparently reached their saturation point for this operation.

In Run 5, much less chromium was adsorbed than in the previous cycles. This was due either to channeling or the residual loading from previous runs, not because of the saturation limits alluded to in the previous cycles. In this cycle, 3.91 pounds of the chromium left on the carbon from the previous cycle was removed in addition to the 4.16 pounds adsorbed during this cycle (100 percent recovery). During the desorption treatment, the chelating agent concentration was increased 8 times without any change in total recovery.

In Run 6, the chromium adsorbed increased, but not to the level of Cycle 4, probably because of the milder acid pretreatment (dropwise addition). Again all the adsorbed chromium from this run was recovered plus 1.46 pounds from previous runs. The combined caustic-solution wash and the water wash accounted for 98 percent of the chromium recovered. The concentration of the caustic solution was 25,374 ppm of Cr and the water wash concentration was 11,226 ppm of Cr. Both these concentrations are close to the maximum concentration of 29,500 ppm Cr and 13,400 ppm Cr for caustic and water solutions, respectively, encountered in the eight cycles of regeneration (see Figure 8).

In Runs 7 and 8, the operation stabilized with 98 percent of the adsorbed chromium recovered (59 percent in the caustic - 39 percent in the water wash). The chromium remaining in the 200 pounds of carbon stabilized to 6.82 pounds (see Figure 9).

These data suggest that a large number of cycles could be repeated before the carbon is spent.

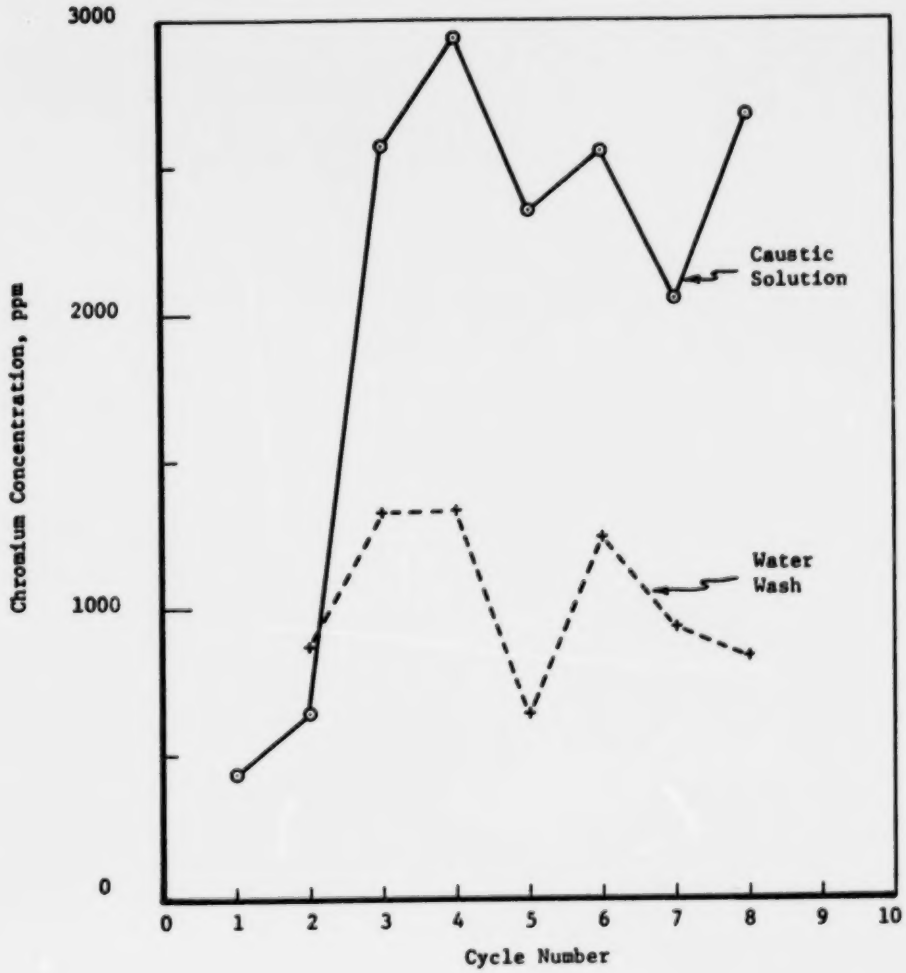

FIGURE 8. CONCENTRATION OF CHROMIUM IN WASH SOLUTIONS

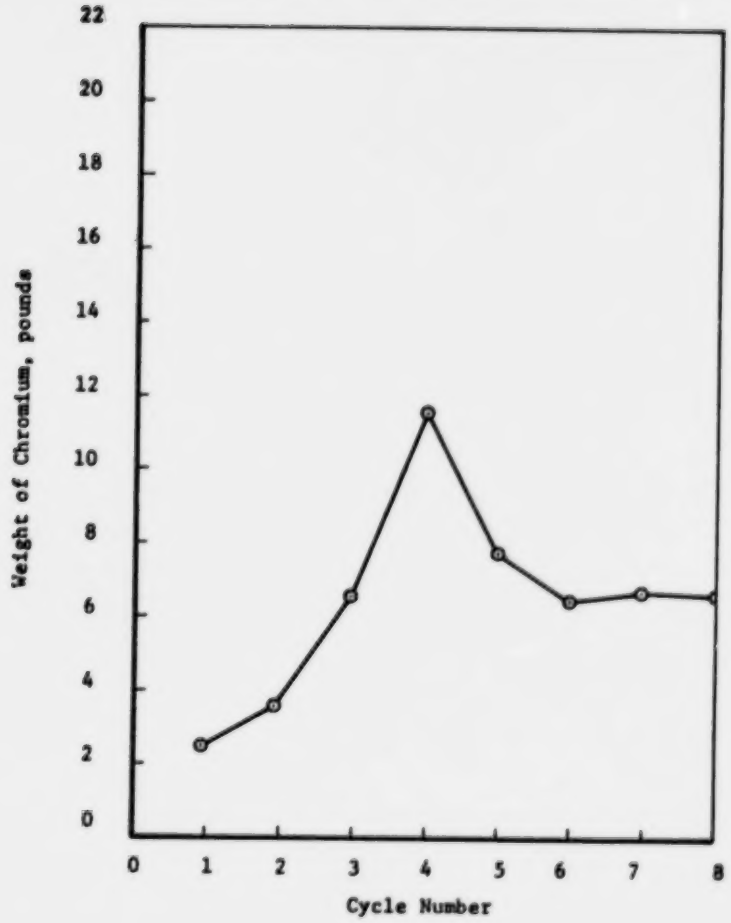

FIGURE 9. CHROMIUM LOADING REMAINING ON CARBON AFTER REGENERATION

During Cycle 8 the effluent was recycled to the rinse tanks for several hours without injury or damage to the plated products.

The adsorption portion of the cycle was routine. The condition found most detrimental to successful operation was bubble formation in the column. This caused channeling and led to premature termination of the adsorption. For this reason upflow filling of the column is suggested. The quantity of chromium adsorbed during these runs appeared to be dependent on the manner acid additions were made, i.e., slow additions suggest a low adsorption and fast additions suggest a high adsorption.

Ideally whatever is adsorbed is desorbed. However, the forces involved in the two operations work in an opposite manner and so the adsorption bonding force must be broken to desorb. In this system it was found that aeration after wetting of the chromium with caustic was helpful in achieving desorption. However, as the chromium was removed in an upflow direction (opposite to adsorption, which was in a downflow direction), it was put back (recycled) into the bottom of the column where it might be readsorbed. This suggests a once-through washing of the column at least for the first portion of the caustic regeneration cycle.

The maximum concentration of desorbed chromium in the caustic solution encountered in the eight cycles was 29,500 ppm (see Figure 8). This suggests that a limit may have been reached, and also suggests that a second caustic wash with fresh solution may have removed additional chromium in Cycle 4 (see Figure 9).

The water wash following the 20 percent caustic wash removed about half as much chromium as the caustic wash. This suggests that the concentration of caustic may have a considerable effect on chromium desorption. Chromium concentration in the water wash as shown graphically in Figure 8 indicates that the solubility limit was reached.

The acid wash is a complicated step in the operation and although only a small portion of the chromium adsorbed is removed in this step, the change from a pH of 11.5 to 3.0 is accompanied by changes in the solution. As the pH decreases, first the color of the solution changes from yellow to orange; next, at pH 8.3, a precipitate appears. At lower pH (6.1) the precipitate disappears and an orange solution appears accompanied at a lower pH by a green precipitate.

With regard to the behavior of the carbon, no detectable loss of carbon occurred during the pilot-plant operations. All solutions run through the carbon were sampled, tested, or analyzed at various times. No carbon particles were detected visually in any of the samples or on filter paper catches. It was concluded that carbon losses were so small as to be undetectable in terms of the 200-pound charge, the residual chromium, and the effects of moisture content pick-up which would occur during any removal and handling of the carbon.

Capital and Operating Cost Estimates for the Removal of Hexavalent Chromium from Plating Rinse Waters

For the removal of chromium from rinse water via the activated carbon adsorption process the following conditions have been assumed:

Flow rate of waste rinse water	20 gpm
Hexavalent chromium concentration	100 ppm
Loading of activated carbon	4% by weight
Number of cycles possible before discard	50
Bulk density of carbon	30 lbs/ft^2
Carbon required for 1 day's operation	600 lbs
Size of column of activated carbon required for above	20 cu. ft.
Assumed dimensions of column total	2.50' dia. x 6'
Number of columns (1 working, 1 polishing, 1 on regeneration)	3
Total weight of carbon in columns	1800 lbs
Additional tankage	
Equalizing tank	600 gallons
Discharge tank	600 gallons
NaOH tank for regeneration	250 gallons
Pumps	
Feed pump to columns	1 hp
Circulating pump for regeneration	1 hp
Circulating pump for discharge tank	1 hp
Treatment tank for Na_2CrO_4 solution	250 gallons

Capital and operating costs based on these assumptions are shown in Tables 2 and 3, respectively.

It further is assumed that the regenerant containing the chromium will be removed on a scheduled basis by an industrial waste disposal contractor. Preliminary estimates indicate that the cost of disposal in this manner will amount to about $17.50 per day. This will increase the daily operating cost to about $62.60.

TABLE 2. CAPITAL COSTS FOR ACTIVATED CARBON PROCESS

No.	Items of Equipment	Specifications	Unit Cost	Estimated Costs
3	Absorption Towers	2.5' dia. x 8' overall, rubber lined, fitted with distributor's piping valves gauging. Charged with carbon Installed		$25,000[1]
2	Auxiliary Tanks	Feed and discharge 600 gallons, installed		4,000
1	Caustic Feed Tank	250 gallons, installed		700
1	Treatment Tank for Na_2CrO_4	250 gallons, installed		700
3	Pumps	14 p each, installed	650	1,950
3	Pump Motors		150	450
	Miscellaneous Piping			2,000
	Miscellaneous Electrical			1,000
TOTAL				$35,800

1 Informal estimate, not quotation from information in manufacturer's literature.

TABLE 3. ESTIMATED OPERATING COSTS FOR CARBON ADSORPTION PROCESS

	Basis	Unit Cost, dollars	Daily Costs, dollars[1]
Direct Costs			
Reagents			
Sulfuric Acid	100 lbs/day	0.03	$ 3.00
Sodium Hydroxide	150 lbs/day	0.06	9.00[2]
Carbon Losses	12 lbs/day	0.30	3.60[3]
Labor	2 mans/hours/day	4.00	8.00[4]
Maintenance	5% of fixed capital cost	-	5.00
Plant Supplies	15% of above	-	1.00
Utilities, Power, etc.	-	-	2.50
Direct Cost/Day			$32.10
Fixed Costs			
Depreciation, Taxes, Insurance			13.00
Direct plus Fixed Costs			$45.10

1 Assuming the Na_2CrO_4 is used in the plating plant, e.g., anodizing, or hauled away by a chemical reclaimer at no cost.

2 NaOH in regenerating solution.

3 Assumes complete replacement of carbon is necessary every 50 cycles. 60 lbs/50 = 12 lbs/day.

4 Includes labor required for operation of adsorption unit regeneration.

References

(1) "A State-of-the-Art Review of Metal Finishing Waste Treatment", U.S. Department of the Interior, Federal Water Quality Administration, Water Pollution Control Research Series, 12020 EIE 11/68, Washington, D.C.

(2) "An Investigation of Techniques for Removal of Chromium from Electroplating Wastes", U.S. Environmental Protection Agency, 12010 EIE 03/71, Washington, D.C.

(3) "An Investigation of Techniques for Removal of Cyanide from Electroplating Wastes", U.S. Environmental Protection Agency, 12010 EIE 11/71, Washington, D.C.

SECTION V

APPENDIXES

		Page
A.	Methods Used for Control Analyses	33
B.	Summary Data from Laboratory Experiments	36
C.	Summary of Regeneration Operation Data	39
D.	Data on Results of Eight Cycles on Operation of the Pilot-Plant Unit	43

APPENDIX A

METHODS USED FOR CONTROL ANALYSES

Simplified Test for Hexavalent Chromium

(1) Transfer a 50-ml sample, containing no more than 1.25 ppm of hexavalent chromium (predilute if necessary) to a 100-ml Erlenmeyer flask.

(2) Add 0.1 gram of solid reagent mixture made by grinding together 0.25 gram of 1,5 diphenylcarbohydrazide and 9.75 grams of tartaric acid.

(3) Shake vigorously until all the reagent is dissolved.

(4) Let stand 5 minutes to develop full color and measure the absorbance in a spectrophotometer at 540 m wavelength.

(5) Determine the hexavalent chromium concentration of the solution by comparison with a standard calibration curve (see Figure A-1).

(6) The color also may be compared against a set of permanent standards prepared in steps of 0.5 ppm by mixing together various proportions of cyrstal violet and safrinin.

This simplified test was taken from the reference "Simplified Test for Hexavalent Chromium" by B. L. Goodman in Water and Sewage Works, February, 1961, (page 80). It may be noted that the referenced publication makes no mention of the maximum time of standing [cf (4) above] before before the fading of the color. In the performance of these analyses on this program good practice was observed in all aspects of analytical procedure. For example, blanks of tap water and analytical standards were run in association with analyses of chrome-rinse waters. Checks among the blanks and standards were so close as to indicate no interference or variance other than routine. An examination of the referenced publication would indicate this method gives a precision of 11 parts in 1000 parts at a chromium concentration of one ppm and had an average accuracy within 2 percent of the complete Standard Method as given in "Standard Methods for the Examination of Water, Sewage, and Industrial Wastes", APHA, AWWA & WPCF, New York, 10th ed., 1955. Examination of the publication describing the simplified method shows that the article states that the "permanent standards are absolutely stable", in terms of checks against spectrophotometric analyses over a period of a year and a half.

All determinations of pH were made using commercial bench-type pH meters for research work, with the meters standardized before each use and periodically calibrated against National Bureau of Standards standards according to BCL's routine instrument calibration schedules and procedures. All sampling and handling techniques were in accordance

with the "Standard Methods" referenced above or in accordance with analytical procedures developed by BCL depending on which would give better results on this program.

Titrimetric Method for Total Chromium

A control procedure for total chromium also was developed. This method involved the oxidation of chromium by ammonium persulfate in the presence of silver nitrate and titration of the chromium by the conventional ferrous sulfate-permanganate titration.

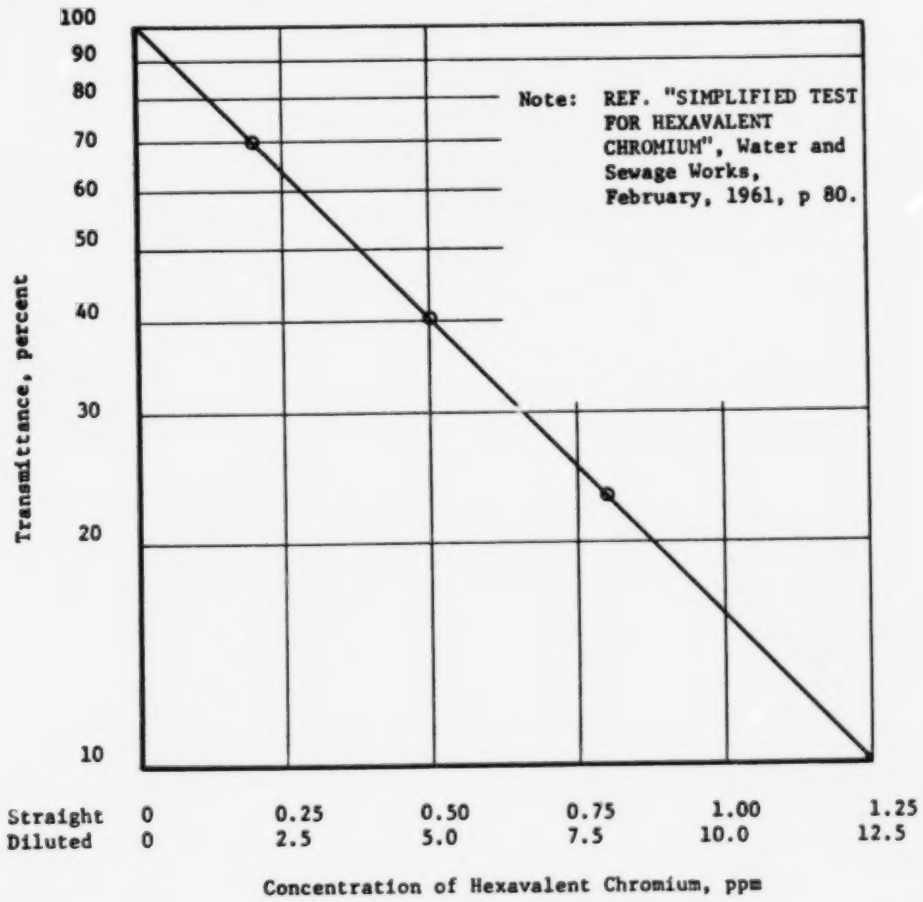

FIGURE A-1. STANDARD CHROMIUM CURVE

APPENDIX B

TABLE B-1. SUMMARY OF DATA FROM LABORATORY EXPERIMENTS ON CHROMIUM ADSORPTION AND REGENERATION USING ACID AND BASIC MEDIA

Experiment No.	Stripping Solution	Cycle	Initial Solution Total Cr, grams	Adsorbed Total Cr, grams	Adsorbed Total Cr, percent	Total Chromium Adsorbed, grams Cr/gram carbon	Total Chromium Remaining on Carbon, cumulative grams Cr/gram carbon
1	5% H_2SO_4	1	0.234	0.194	82.9	0.0388	0.0120
1		2	0.234	0.168	71.8	0.0336	0.0230
1		3	0.234	0.141	60.3	0.0282	0.0200
1		4	0.297	0.151	50.8	0.0302	0.0260
1		5	0.297	0.142	47.8	0.0284	0.0275
2	5% H_2SO_4 +	1	0.297	0.236	79.4	0.0472	0.0108
2	10 g/l EDTA	2	0.297	0.218	73.4	0.0436	0.0182
2		3	0.297	0.225	74.8	0.0450	0.0388
2		4	0.297	0.200	67.3	0.0400	0.0388
2		5	0.297	0.163	54.9	0.0326	0.0582
2		6	0.315	0.113	35.9	0.0226	0.0616
2		7	0.315	0.141	44.8	0.0282	0.0780
2		8	0.310	0.066	21.3	0.0132	0.0568
2		9	0.310	0.130	42.0	0.0260	0.0698
3	5% H_2SO_4 +	1	0.297	0.241	81.1	0.0482	0.0235
3	10 g/l	2	0.297	0.146	49.1	0.0292	0.0304
3	ammonium	3	0.297	0.101	34.0	0.0202	0.0334
3	persulfate	4	0.297	0.083	27.9	0.0166	0.0348
3		5	0.297	0.085	28.6	0.0170	0.0382
4*	20% NaOH	1	0.297	0.234	78.7	0.0468	0.0065
4		2	0.297	0.219	73.8	0.0438	0.0095
4		3	0.297	0.217	73.1	0.0434	0.0167
4		4	0.297	0.207	69.7	0.0414	0.0132
4		5	0.297	0.189	63.6	0.0378	0.0115

TABLE B-1. (Continued)

Experiment No.	Stripping Solution	Cycle	Initial Solution Total Cr, grams	Adsorbed Total Cr, grams	Adsorbed Total Cr, percent	Total Chromium Adsorbed, grams Cr/gram carbon	Total Chromium Remaining on Carbon, cumulative grams Cr/gram carbon
5	5% $(NH_4)_2CO_3$	1	0.297	0.236	79.4	0.0472	0.0213
5		2	0.297	0.208	70.0	0.0416	0.0305
5		3	0.312	0.211	67.6	0.0422	0.0345
5		4	0.312	0.194	62.2	0.0388	0.0351
5		5	0.312	0.114	36.5	0.0228	0.0354
6	20%	1	0.312	0.246	78.8	0.0482	0.0149
6	NaOH +	2	0.312	0.232	74.4	0.0464	0.0175
6	10g/l EDTA	3	0.312	0.227	72.8	0.0454	0.0289
6		4	0.312	0.226	72.5	0.0452	0.0318
6		5	0.312	0.224	71.8	0.0448	0.0300
7	20% NaOH	1	0.305	0.239	78.4	0.0478	0.0181
7	+ 5g/l EDTA	2	0.305	0.198	64.9	0.0396	0.0121
7		3	0.305	0.213	69.8	0.0426	0.0218
7		4	0.305	0.206	67.5	0.0412	0.0204
7		5	0.305	0.204	66.9	0.0408	0.0202
8*	20% NaOH	1	0.305	0.230	75.4	0.0460	0.0111
8	+ 1 g/l EDTA	2	0.305	0.218	71.5	0.0436	0.0086
8		3	0.305	0.203	66.6	0.0406	0.0063
8		4	0.305	0.208	68.2	0.0416	0.0099
8		5	0.305	0.203	66.6	0.0406	0.0112
9	20% NaOH	1	0.315	0.274	86.9	0.0547	0.0112
9	+0.5 g/l EDTA	2	0.315	0.214	67.4	0.0425	0.0161
9		3	0.315	0.194	61.6	0.0388	0.0161
9		4	0.315	0.200	63.4	0.0399	0.0195

TABLE B-1. (Continued)

Experiment No.	Stripping Solution	Cycle	Initial Solution Total Cr, grams	Adsorbed Total Cr, grams	Adsorbed Total Cr, percent	Total Chromium Adsorbed, grams Cr/gram carbon	Total Chromium Remaining on Carbon, cumulative grams Cr/gram carbon
10	20% NaOH	1	0.315	0.274	86.9	0.0547	0.0042
10	+ 0.25 g/l	2	0.315	0.205	65.0	0.0410	0.0039
10	EDTA	3	0.315	0.207	65.6	0.0413	0.0117
10		4	0.315	0.177	56.2	0.0354	0.0131
10		5	0.315	0.201	63.8	0.0402	0.229
11	20% NaOH	1	0.315	0.251	79.8	0.0502	0.0071
11	+ 0.1 g/l	2	0.315	0.232	73.8	0.0465	0.0163
11	EDTA	3	0.315	0.220	69.9	0.0441	0.0097
11		4	0.315	0.208	66.0	0.0416	0.0109
11		5	0.315	0.200	63.6	0.0400	0.0135

* See Table 1 for additional cycles.

APPENDIX C

TABLE C-1. SUMMARY OF REGENERATION OPERATION DATA

Operation	PPM Hexa Chromium	PPM Total Chromium	Actual Volume, gallons	Estimated Volume, gallons	Actual Weight of Chromium, pounds	Estimated Weight of Chromium, pounds	Comments *
Cycle 1							
(1) First caustic solution 1/2 hour after cycling	3,300	4,052	--	30	--	1.01	Chromium removed in first 1/2 hour
(2) First caustic solution 100 hours after cycling	4,250	5,255	22.5	--	0.987	--	Additional 4 days no help
(3) Second caustic solution 1/4 hour after cycling		1,731		37.5		0.54	
(4) Second caustic solution 72 hours after cycling	2,550	2,845	12.5		0.296	--	Little chromium removed by second caustic wash
Ditto	1,675	1,862	60	--	0.932	--	
(5) Wash water solution 2 hours after after cycling	160	--	9	--	0.013	--	
(6) Wash water solution 3 hours after after cycling	325		30		0.009		
(7) H_2SO_4 wash 1 hour after cycling	--	--		30	--	0.53	
(8) H_2SO_4 wash 72 hours after cycling pH 2.3			7.5		0.457		
(9) H_2O wash 2 hours after cycling			60		2.73		Most of chromium removed in water wash after pH adjustment
(10) H_2O wash and acid pH adjustment			34		0.063		
Cycle 2							
(1) Caustic solution 24 hour recycle							
(2) Aerate for 24 hours							
(3) Caustic solution drained after 1 hour cycle	6,200	6,311	30	--	1.58	--	Good removal after aeration. Air must oxidize chromium.
(4) Water wash 1 hour recycle	8,750	8,891	30	--	2.22		Good removal with water wash
(5) Acid wash 22 hour recycle (pH 1.8 adjust to 3.0 with NaOH)		1,807	26		0.39		
(6) Water wash 1 hour recycle		1,166	30		0.29		
Cycle 3							
(1) Caustic solution 1/4 hour recycle		15,580	--	30	--	3.90	
(2) Aerate for 18 hours		--	--	--	--	--	
(3) Caustic solution 1/4 hour recycle		27,417		30		6.86	
(4) Caustic solution continued for 8 hours		25,331		30		6.34	

* Note: All caustic solutions contain 20% NaOH plus 500 ppm EDTA unless otherwise noted.

TABLE C-1. (Continued)

Operation	PPM Hexa Chromium	PPM Total Chromium	Acutal Volume, gallons	Estimated Volume, gallons	Actual Weight of Chromium, pounds	Estimated Weight of Chromium, pounds	Comments
(5) Aerate over weekend (72 hours)		--		--		--	
(6) Caustic solution 1/4 hour recycle		25,200		30		6.30	
(7) Continued caustic solution 9 hour recycle							
(8) Aerate 16 hours							
(9) Caustic solution 1/4 hour recycle		25,765	33	--	7.09	--	About 100 percent more chromium removed with aeration step involved
(10) Water wash 2 hour recycle	13,140	13,012	31	--	3.36	--	About 50 percent as much chromium removed in water wash as in preceding caustic wash
(11) Acid wash 6 hour recycle pH 3.4		1,506	76	--	0.95	--	
(12) Water wash		Combined with acid wash					
Cycle 4							
(1) Caustic solution 1/2 hour recycle, drain		18,560	--	30	--	4.64	
(2) Aerate for 24 hours		--		--		--	
(3) Caustic solution 1/2 hour recycle		29,495	29	--	7.13	--	Same comments as for Cycle 3
(4) Water wash 1/2 hour recycle	13,400	12,969	28	--	3.03	--	
(5) Added water and H_2SO_4 slow addition pH 3.0		1,426	29	--	0.35	--	
(6) Water wash 1 hour		1,607	15		0.20		
Cycle 3							
(1) Caustic solution 4-1/2 hours recycling		10,627		30		2.66	
(2) Aerate overnight		--		--		--	
(3) Caustic solution 1/2 hour recycle		19,822		30		4.96	
(4) Added 480 grams EDTA-4 percent recycle 1/2 hour		19,822		30		4.96	Chelating agent did not remove chromium
(5) Caustic solution 1/2 hour recycle	19,500	20,343	24	--	4.10	--	
(6) Water wash once through left column Water wash recirculating right column	3,100 6,400	3,099 6,302	60 30		1.55 1.58		Note last portion of water through the column analyzed 39 ppm chromium
(7) Acid wash - right column pH 3.1 Acid wash - left column pH 2.4		1,062 2,370	26.5 30.5		0.24 0.60		

TABLE C-1. (Continued)

Operation	PPM Hexa Chromium	PPM Total Chromium	Actual Volume, gallons	Estimated Volume, gallons	Actual Weight of Chromium, pounds	Estimated Weight of Chromium, pounds	Comments
Cycle 6							
(1) Caustic solution 1/2 hour recycle		11,711		30		2.93	
(2) Aerate 18 hours							
(3) Caustic solution 1 hour recycle		21,080		30		5.27	
(4) Aerate 8 hours							
(5) Caustic solution 1-1/2 hour recycle		22,121		30		5.53	
(6) Aerate 72 hours							
(7) Caustic solution 1/2 hour recycle		26,459		30		6.62	
(Final)		25,374	35	--	7.41		
(8) Water wash recycle 1 hour	12,200	11,226	25	--	2.34	--	
(9) Acid wash recycle 2 hours (acid addition slowly) pH 3.1 6 liters/80 minutes		722	35	--	0.21	--	
(10)							
Cycle 7							
(1) Caustic solution 1 hour recycling (with air sparging)		10,887	--	30	--	2.73	
(2) Aerate for 18 hours + 1/2 hour caustic solution recycle		17,524		30		4.39	
(3) Caustic solution 8 hour recycling		18,434		30		4.61	
(4) Aerate 28 hours		--		--		--	
(5) Caustic solution 1/2 hour recycle	20,000	20,300	30.5	--	5.17	--	
(6) Water wash - left column 15 gallons 5 minute recyle		11,234		15		1.40	
- right column 15 gallons 5 minute recycle (combined and used in)--		20,647		15		2.58	
- left and right columns 30 gallons - 15 minute recycle	8,980	9,022	30	--	2.11	--	
(7) Water wash 1/4 hour recycle	4,060	4,075	34	--	1.15	--	
(8) Acid wash-acid added slowly to water-after water added		1,815		30		0.45	
-after 2.5 ℓ conc. acid added (left column only)		739		30		0.19	
-after 4.5 ℓ conc. acid added		6,011		30		0.02	
-after 60 ℓ conc. acid added-total addition in 1 hour							
(9) Recycle acid for 5 hours and leave in column 72 hours pH 2.7		503	26		0.11		

TABLE C-1. (Continued)

Operation	PPM Hexa Chromium	PPM Total Chromium	Actual Volume, gallons	Estimated Volume, gallons	Actual Weight of Chromium, pounds	Estimated Weight of Chromium, pounds	Comments
Cycle 8							
(1) Caustic solution wash - 15 minute recycling	24,750	26,806		30		6.71	Green color in solution after 5 minutes
(2) Aerate for 15 hours							
(3) Caustic solution wash - 2 hours with sparging air-one column	9,933	9,700[a]		30		2.49	
-2 hours with sparging air-both columns	17,200	18,001	31.5		4.73		
(4) Water wash 3/4 hour	8,000	8,137	30		2.04		
(5) Water wash - left column	6,270	6,558	15		0.82		
- right column	5,250	5,517	15		0.69		

(a) One air pump not operating.

APPENDIX D

TABLE D-1. DATA ON RESULTS OF EIGHT CYCLES OF OPERATION IN THE PILOT-PLANT UNIT

Cycle Number	Adsorption Time, hours	Weight of Chromium Adsorbed, pounds	Weight of Chromium Recovered, pounds	Weight of Chromium Not Recovered, pounds	Weight of Chromium on Carbon From all Previous Cycles, pounds	Total Weight of Chromium on Carbon (Loading)	Chromium on Carbon After Regeneration, percent or g/100 g carbon	Chromium on Carbon After Adsorption, percent	Weight of Chromium Removed in Caustic Wash, pounds	Weight of Chromium Removed in Water Wash, pounds	Weight of Chromium Removed in Acid Wash, pounds	Weight of Chromium Removed in Water After Acid Wash, pounds	Chromium Removed by NaOH Wash, percent of Cr recovered	Chromium Removed by Water Wash, percent of Cr recovered	Chromium Removed by Acid Wash, percent of Cr recovered	Chromium Removed by Final Water Wash, Percent of Cr recovered	Chromium Not Recovered, percent
1	11-3/4	8.16	5.49	2.67	2.67	8.16	1.32	4.08	1.28	0.954	4.57	2.79	23.4	17.4	8.32	50.9	48.6
2	20	5.46	4.48	0.97	3.64	8.13	1.82	4.07	1.58	2.22	0.39	0.29	35.3	49.6	9.0	6.5	21.6
3	19-1/2	14.12	11.40	2.72	6.36	17.76	3.18	8.88	7.09	3.36	0.95	--	62.2	29.5	8.0	--	23.8
4	30-1/4	16.11	10.71	5.40	11.76	22.47	5.83	11.24	7.13	3.03	0.35	0.20	66.6	28.3	3.3	0.7	50.4[a]
5	19-1/2	4.16[c]	8.07	(3.91)	7.85	15.92	3.93	7.96	4.10	3.13	0.84	--	50.8	38.8	10.4	--	[b]
6	14	8.50	9.96	(1.46)	6.39	16.35	3.19	8.18	7.41	2.36	0.21	--	74.4	23.5	2.1	--	--
7	14-1/4	8.98	8.56	0.44	6.83	15.37	3.41	7.68	5.17	3.26	0.11	--	60.5	38.2	1.3	--	0.52
8	13-1/2	8.26	8.26	0.02	6.81	--	3.41	--	4.73	3.55	No acid wash	--	57.1	42.9	0	--	0.25

(a) Removed in Cycle 5.

(b) Removed in Cycle 6.

(c) Chromium broke through one column after 5 hours operation--probably channeling.